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Criteria for Evaluating the Reliability of Literature Data on Environmental Process Constants

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In the assessment of health risk from pollutant exposure, it is important for the modeler to know the degree of confidence he/she can have in literature values that are needed for estimating the fate of toxic substances in the environment. Since literature values, in general, are of unknown reliability, evaluation criteria were developed for twelve rate and equilibrium constants used in environmental modeling. The evaluation criteria also can be used to assess the reliability of literature values for other properties.

KEY WORDS: Health risk, pollutant exposure, literature values.

INTRODUCTION

Scientists and engineers who are engaged in the assessment of health risk from pollutant exposure, the development of exposure assessment models, or the development of predictive techniques for estimating physical and chemical properties need data on chemicals that enter the environment. The U.S. Environmental Protection Agency's Office of Toxic Substances, for instance, is required under the Toxic Substances Control Act to assess the potential adverse

impact of chemicals as they are first proposed for manufacture and of chemicals that have been manufactured for some time. The quickest and least expensive way of accessing data is through a computerized database of chemical properties.

Over the past 15 years, several mathematical models have been developed that predict the concentrations existing at various points in the environment resulting from introduction of toxic chemicals. These models include expressions describing the various physical, chemical, and microbiological processes by which chemicals may be transformed or transported. Other techniques are used for estimating the fate of chemicals that compare the chemical of interest to similar chemicals whose properties are already known. In each case of estimation, it is necessary to use reliable transformation rate constants.

Thousands of toxic chemicals must be assessed for their potential environmental impact; however, there is a paucity of required transformation and equilibrium constants in the literature, and the published data are often of unknown quality. This problem results primarily from the fact that most literature data were obtained in mechanistic research in which absolute and precise values were not the major objective of the studies. It is necessary, then, to develop and apply methods to measure chemical rate and equilibrium constants that the user can apply with confidence and to establish a database containing chemical and physical constants of evaluated quality that enhance the users' abilities to predict transport and transformation of toxic chemicals. Data being used in the environmental and human risk assessment for regulatory purposes must be of known reliability for the assessment to have validity.

Good measurements are clearly important in providing data that insure a quality environment and health to the public. But measurements are not the only feature that provide this insurance. The entire experimental scheme is important, including planning and proper protocol; sampling requirements; experimental design set up, and chemical analysis; handling of data, and a sound quality assurance program. Whatever the purpose of measurement, whether for the determination of concentration and/or fate of the chemical in the environment, or for use in environmental risk assessments and ultimately regulatory decisions, the accuracy of the entire measurement process must be insured by the investigator.[1]

Literature values vary, sometimes considerably,[2,3] and data evaluation systems have been suggested[3-5] to address the problem. The users of these varying values, especially mathematical modelers, need to know which values are the most reliable. Because the original investigator is the only one who can actually ensure the accuracy through application of a proper experimental program, the reliability of any literature value can only be evaluated through the research report provided by the author or authors.

It was the objective of this investigation to develop such an evaluation system of the reliability of literature values on environmental rate and equilibrium constants of organic chemicals. An environmental properties database presently under development at the Environmental Research Laboratory, Athens, GA, will include reliability evaluations for all entries.

Evaluation criteria were developed for 12 rate and equilibrium constants:

- —ionization (pK_a)
- —Henry's law constant (H_c)
- —vapor pressure (P_v)
- —water solubility (S_w)
- —sediment/water partition coefficient (K_p)
- —organic carbon normalized sediment/water partition coefficient (K_{oc})
- —octanol/water partition coefficient (K_{ow})
- —direct (aqueous) photolysis rate constant (k_d)
- —aqueous photolysis reaction quantum yield (ϕ_r)
- —molar absorptivity (ε_λ)
- —hydrolysis rate constant (k_h)
- —biotransformation rate constant (k_{bio}).

To create an evaluation system for environmental properties, a data reliability indicator was established to provide a numerical rating. This numerical rating is based on both common and property-specific evaluation criteria.

THE DATA RELIABILITY INDICATOR (DRI)

Confidence in a measured value is influenced by the design of the

experimental procedure and how well this procedure is actually followed in the laboratory. The relative importance of error sources varies with measurement methods and with purity of chemicals. It is important to remember that data collected in a database are removed from the original report, and the errors, therefore, can only be evaluated by consulting the original report. Evaluated data should be valuable because most users are not familiar with the measurement procedures and, therefore, cannot effectively evaluate the data.

It is important in predicting the fate of toxic substances to know the reliability of the data needed, especially when these predictions are used for exposure assessments. In as much as it is practically impossible to evaluate a report and come up with a number that indicates the accuracy of a value, the goal in developing these evaluation criteria was to indicate reliability based on all the information provided in the report and on available corroborative information. The Data Reliability Indicator (DRI), as used here, is defined as the degree of confidence with which a literature value can be used.

The goal of data evaluation is to determine the confidence one can have in the measurement process. Although the need for reliable data for assessment purposes is evident, evaluating literature data with any kind of system is not easy. There is no statistical approach for evaluating confidence in literature data and even with objective evaluation criteria, evaluations require expertise and judgment of the data evaluator. Moreover, the approach and techniques for evaluating data will vary depending on the process constant or property measured. The difficulty in assessing individual measurements, then, makes the evaluation of data a difficult task. Evaluating data can be reasonably objective, however, if the method and experimental procedures used in the measurement process are adequately described in the literature. If important information is not reported, the evaluator must still attempt to estimate the reliability of the reported value. It is important, therefore, that the evaluation of data reliability is performed by persons familiar with the processes or properties of interest.

To establish a data evaluation system, a set of criteria was developed to produce a consistent and defined assessment process. These criteria make certain that all important issues are evaluated

and that the judgment and standards of those who have expertise are incorporated. The criteria are divided into four major categories:

1. Chemical analysis (analytical) information
2. Experimental information
3. Statistical information
4. Corroborative information.

These categories can generally be evaluated independently of each other, although some information may be applied to several categories. It is noteworthy to mention that corroborative information is often not available, and that adequate experimental, analytical, or statistical information is sometimes not provided by authors. Whatever the reason, if information is missing, the value's assessed credibility will decrease.

1. To evaluate *analytical information*, one must determine whether an appropriate analytical method was used and whether the method was suitable for the particular chemical. Many analytical methods are well established and have been recognized as acceptable. Other methods require special equipment and expertise that is not available to many laboratories. Most literature data, however, have been obtained using analytical methods that have been found adequate, and evaluators can objectively judge the data if the method is well described. If the method was not established previously, then the publication describing the measurement must contain sufficient information to establish the validity of the analytical method. This is followed by an evaluation of other analytical information such as product interferences, detection limits, calibration conditions, and extraction efficiency.

2. To evaluate *experimental information*, one must screen the entire methodology. Authors should provide information on controls and calibration of instrumentation in a manner that enables others to repeat the experiment. Issues like temperature, pH, time, replication, and characterization of media should be considered. The purity of the chemical under study should be stated, and whether the chemical transforms by other processes. The chemical's identity should be established; the name on the label of the chemical's container is not proof of identity. The source of the chemical and any purification performed should be part of the discussion. One way of insuring the

proper functioning of the entire experimental methodology is to test a reference chemical of known value in addition to the test chemical.

3. To evaluate *statistical information*, one must know the replicability of a measurement. Every measurement is subject to a degree of uncertainty that, at best, can be reduced only to some acceptable level. The determination of this level is up to the judgment of the researcher who must always make a compromise between higher accuracy and greater expenditure of effort. Besides showing the accuracy of a datum, the researcher must also show the precision to describe the reproducibility of results. The reproducibility should be shown for each sample set up and for independent replicate sample set ups.

4. To evaluate *corroborative information*, one must substantiate the quality of a measured value with results from an independently conducted study. This might be obtained by another independent method, perhaps in another laboratory, or by applying different experimental conditions. Corroboration also may be obtained through property-reactivity correlations.[6]

The DRI for the value of a constant will be a composite of the four major criterion categories: analytical ($\bar{A}$), experimental ($\bar{E}$), statistical ($\bar{S}$) and corroborative ($\bar{C}$). Each major criterion category is composed of subcriteria. The subcriteria consist of a number of questions to be answered with yes or no by the evaluator. This number of questions varies from property to property. The questions are structured in such a way that the more yes answers given for a major category, the higher the reliability of the value of this major category will be. Each subcriterion has been assigned a weight from 1 to 5, where increasing values indicate increasing importance of a subcriterion. To calculate the DRI for each major criterion category, the values of all yes answered questions are added and divided by the sum of the maximum possible values regardless of yes or no answers. This normalized DRI will be a number between zero and one. The following equations are used.

$$\bar{A} = \sum_{i=1}^{n} A(\text{yes})_i \Big/ \sum_{i=1}^{m} A(\text{max})_i$$

$$\bar{E} = \sum_{i=1}^{n} E(\text{yes})_i \Big/ \sum_{i=1}^{m} E(\text{max})_i$$

$$\bar{S} = \sum_{i=1}^{n} S(\text{yes})_i \Big/ \sum_{i=1}^{m} S(\text{max})_i$$

$$\bar{C} = \sum_{i=1}^{n} C(\text{yes})_i \Big/ \sum_{i=1}^{m} C(\text{max})_i$$

COMMON EVALUATION CRITERIA

The questions that make up the common evaluation criteria, with their numerical rating, are listed below for the major criterion categories.

Analytical information:

(4) Is analytical method recognized as an acceptable method?
(5) Could you repeat the analytical part with the available information?
(3) Was the chemical analyzed within the linear range of the instrumentation?
(2) Is detection limit stated?
(4) Was either HPLC or GC used?
(3) Is extraction efficiency stated (% recovery, ignore if HPLC was used and extraction was not done)?
(3) Was high purity solvent used for extractions (ignore if extraction was not done)?
(2) Were product interferences checked for?

Experimental information:

(5) Could you repeat the experiment with the available information?
(1) Is a clear objective stated?
(2) Is water quality characterized or identified (distilled or deionized)?
(3) Are results presented in detail, clearly and understandably?
(3) Are data from a primary source and not from a referenced article?
(5) Was the chemical tested at concentrations below its water solubility?
(2) Were particulates absent?
(3) Was a reference chemical of known constant tested?

(5) Were other fate processes considered?
(3) Was a control (blank) run?
(5) Was temperature kept constant?
(3) Was the experiment done near room temperature (15–30 °C)?
(3) Is purity of the test chemical reported ($\geqq 98\%$).
(3) Was the chemical's identity proven?
(1) Is source of the chemical reported?

Statistical information:

(3) Were replicate samples analyzed?
(3) Were replicate sample systems run?
(3) Is precision of analytical technique reported?
(3) Is precision of sample analysis reported?
(3) Is precision of replicate sample systems reported?

Corroborative information:

(5) Was paper peer-reviewed?
(3) Do independent lab data confirm results?
(2) Do estimated data confirm results?

The DRI will be reported as $[\bar{A}, \bar{E}, \bar{S}, \bar{C}]$ and will display the actual value for each major criterion category. This evaluation system thus provides a four-value DRI that defines the reliability of the datum, with each value ($\bar{A}$, $\bar{E}$, $\bar{S}$, $\bar{C}$), respectively, describing the reliability of one area of the total experimental methodology.

PROPERTIES AND SPECIFIC EVALUATION CRITERIA

Ionization Constant (pK_a)

The ionization constant (K_a), also called dissociation constant, indicates the strength of acids and bases and expresses the proportion of the different ionic species of the substance present at a given pH. Because ionization constants are small numbers, it has become customary to use their negative logarithms known as pK_a.

For a monoprotonic substance: $pK_a = pH - \log([A^-]/[HA])$

which is derived from: $K_a = [H^+][A^-]/[HA]$

where A^- is the proton acceptor and HA is the proton donor. When pH equals pK_a, equal amounts of ionized and non-ionized chemical

are present. Several methods are in use for the determination of pK_a.[7]

Suggested unit: unitless.

Specific evaluation criteria for pK_a:

Analytical information: none.

Experimental information: none.

Statistical information:

(4) Were averages calculated by converting logs to antilogs?

Corroborative information: none.

Henry's law constant (H_c)

Henry's Law states that the solution of a gas in a liquid is directly proportional to the pressure of the gas above the liquid at a definite temperature and is given by: $H_c = PX^{-1}$, where P is the partial pressure and X is the mole fraction. Hence, H_c data are often used to calculate vapor pressure and the rate of volatilization.

Two techniques are generally applied for the determination of H_c, a dynamic method and a static method. Under the dynamic approach, a stream of gas is passed through a vessel that contains the chemical of interest in solution. When the concentration of the chemical in the gas stream becomes constant, the observed first-order rate constant for loss of chemical from solution is used with the temperature, the rate of gas flow, and the volume of water in the vessel to calculate H_c.

Under the static approach, the chemical, dissolved in water, is allowed to reach equilibrium with the gas phase in a closed vessel. H_c is then calculated from the measured concentrations of the chemical in both the liquid and gas phases.

Suggested unit: *Pa*

Specific evaluation criteria for H_c:

Analytical information: none

Experimental information:

(5) Was equilibrium demonstrated?

(4) Was the chemical studied at a minimum of two temperatures?
(4) Was the chemical studied at a minimum of two different concentrations?

Statistical information: none

Corroborative information: none.

Vapor pressure (P_v)

Vapor pressure is defined as the pressure exerted by a vapor when a state of equilibrium has been reached between a liquid, solid, or solution, respectively, and its vapor. P_v increases as the temperature increases, and P_v values for certain compounds (e.g. chlorinated benzenes and phenols) can be estimated graphically from the boiling points and the boiling point/vapor pressure relationship for homologous series. P_v data can also be estimated using: $P_v = H_c S_w$, where H_c is Henry's law constant and S_w is water solubility. P_v values are used for the calculation of volatilization rates.

Methods used for the measurement of P_v are: dynamic, static, isoteniscope, vapor pressure balance, and gas saturation.

Suggested unit: *Pa*

Specific evaluation criteria for P_v:

Analytical information: none

Experimental information:

(5) Was equilibrium demonstrated?
(4) Was experiment done at more than 2 temperatures to provide correlation between t and P_v?
(4) Was experiment done at a minimum of 2 different concentrations?

Statistical information: none

Corroborative information: none.

Water solubility (S_w)

Water solubility is defined as the quantity of solute present in a given amount of the saturated solution, at a certain temperature. S_w

of a chemical is an important characteristic for that chemical's potential environmental movement and distribution. A number of processes can be affected by S_w such as adsorption and desorption on soils, hydrolysis, photolysis, oxidation/reduction, and biodegradation. S_w values are often used for estimating Henry's law constant for calculating volatilization rate constants. A good correlation has been established between solubilities of organic compounds and their octanol/water partition coefficients.

When saturating the aqueous phase in measuring S_w, one must exercise great care to avoid the generation of a particulate suspension of the chemical, because this will lead to incorrectly high S_w values. A method to avoid such particulate suspensions consists of coating the chemical on beads that are then placed in a column. A slow flow of pure water through the column will then saturate the water with the chemical.

Suggested unit: $mg\,L^{-1}$

Specific evaluation criteria for S_w:

Analytical information: none

Experimental information:

(5) Was final equilibrium shown over time?
(3) Was the reaction vessel capped?
(4) Was the sample kept in a constant temperature bath?
(4) Was a thermostatted centrifuge used at the same temperature?
(5) Was stability of the chemical in water shown?
(4) Was the chemical studied at a minimum of three temperatures?

Statistical information: none

Corroborative information: none.

Sediment/water partition coefficient (K_p)

The sediment/water partition coeficient for a chemical sorbed to a particular sediment in water is given by:

$K_p = C_s/C_w$ for all chemicals

$K_p = K_{oc} f_{oc} \simeq 0.41\ K_{ow} f_{oc}$ for uncharged chemicals only[8]

where

K_{oc} = organic carbon normalized sediment/water partition coefficient

f_{oc} = fraction organic content (weight basis)

K_{ow} = octanol/water partition coefficient

C_s = concentration of chemical on sediment

C_w = concentration of chemical in water

and $0.41\ K_{ow} \simeq K_{oc}$ is an estimated value.

K_p values can be measured in the laboratory or estimated from K_{oc} values. A common method for measuring K_p is the batch adsorption technique in which a solution of the chemical is mixed in a closed vessel with known amounts of sediment. Periodically, the supernatant liquid is sampled until equilibrium has been established, which may take days. The concentration of the chemical adsorbed to the sediment is then analyzed, where this directly measured amount must equal the loss from solution. Processes like biodegradation, volatilization, photochemical reactions, or adsorption of the chemical to vessel walls must be accounted for with blank runs without sediment.

Because K_p values depend on several factors, sediments should be characterized for pH, organic carbon content, cation exchange capacity, and particle size distribution. Sorption of hydrophilic chemicals (with potentially ionizable functional groups) may be affected significantly by hydrogen-ion concentration (pH), redox potential (E_h), and cation exchange capacity of the sediment. This introduces problems in sediment collection, handling, and storage because these properties vary with aeration and may change irreversibly upon drying.

Suggested unit: $L_{water}(kg_{sed})^{-1}$

Specific evaluation criteria for K_p:

Analytical information: none

Experimental information:

(3) Was K_p calculated from slope in the batch method?
(4) Was sediment characterized for *pH*, organic carbon, cation exchange capacity, and size distribution?
(4) Was sediment thoroughly eluted with water before start of experiment?
(3) Were reaction vessels capped?
(4) Is equilibration shown?
(4) Was water/sediment ratio correctly selected to provide sufficient amount for samples?
(4) Was stability of chemical in water/sediment shown?
(3) Was mass balance done?
(3) Was the chemical studied at a minimum of two different concentrations?
(3) Was the chemical studied at a minium of two different temperatures?

Statistical information:

(5) Is plot of C versus t at equilibrium of zero slope?

Corroborative information: none.

Organic carbon normalized sediment/water partition coefficient (K_{oc})

The K_{oc} value for a chemical is given by:

$$K_{oc} = K_p / f_{oc}$$

where

K_p = sediment/water partition coefficient

f_{oc} = fraction organic content (weight basis)

and is used to estimate the K_p value for a sediment of known organic carbon fraction, f_{oc}.

Because K_{oc} values are normalized for the organic carbon content in the sediment, they can be used to estimate K_p values for other sediments. Some researchers use total organic matter for normalization and obtain K_{om} instead of K_{oc}.

K_{oc} values are not measured directly, but are calculated by

dividing f_{oc} into K_p. An HPLC method has been developed, however, to measure K_{oc} values based on retention times similar to the HPLC method for the octanol/water partition coefficient.

Suggested unit: $L_{water}(kg_{org.\,carbon})^{-1}$

Specific evaluation criteria for K_{oc}:

Analytical information: see K_p

Experimental information: see K_p

Statistical information: see K_p

Corroborative information: see K_p.

(Because K_{oc} values are calculated from K_p values, specific evaluation criteria for K_{oc} should be the same as for K_p.)

Octanol/water partition coefficient (K_{ow})

The octanol/water partition coefficient, K_{ow}, is defined as the ratio of the equilibrium concentration of a dissolved substance in a system consisting of *n*-octanol and water, and is ideally dependent only upon temperature and pressure.

$$K_{ow} = C_{oct}/C_w$$

where C_{oct} is the concentration of the substance in *n*-octanol and C_w is the concentration of the substance in water. The K_{ow} is useful in predicting soil adsorption, biological uptake, lipophilic storage, and biomagnification. It is also useful in estimating the organic-carbon normalized sediment/water partition coefficient (K_{oc}) and water solubility (S_w) using property reactivity correlations and is frequently reported in the form of its logarithm to base ten as $\log P$. Estimating transport of chemicals in biological systems using K_{ow} data has been successful. *n*-Octanol is considered similar to lipid and fatty-tissue substances and, therefore, was selected as the organic phase in the measurement of K_{ow}.

Environmental partitioning behavior can best be estimated for organic chemicals with K_{ow}'s between 10^2 and 10^6 (Ref. 9). Chemicals with K_{ow}'s less than 10^2 will not partition well into, or tend to

accumulate in, any hydrophobic compartment whereas chemicals with K_{ow}'s larger than 10^6 will tend to do so.

K_{ow} values are usually obtained by shaking a solute with two immiscible solvents (*n*-octanol and water) and then analyzing the solute concentration in one or both phases (shake and batch method). An indirect HPLC method provides K_{ow} values by using a correlation of the retention times between the chemical in question and other chemicals of known K_{ow} values. Other physico-chemical measurements are done using photometric methods and thin-layer chromatography. EPA has published a method in the *Federal Register*, Vol. 45, no. 227, Friday, November 21, 1980.

Suggested unit: $L_{water}(L_{octanol})^{-1}$

Specific evaluation criteria for K_{ow}:

Analytical information: none

Experimental information:

(2) Is the purity of *n*-octanol reported?
(5) Was octanoic acid removed from octanol by dilute base extraction before distillation?
(3) Were reaction vessels capped?
(4) Is equilibration shown?
(4) Were octanol and water volumes correctly selected to provide sufficient amount for samples?
(3) Was the phase ratio (octanol to water) varied?
(4) Were both phases clear when sampling?
(3) Was mass balance done?
(4) Was the concentration in the water phase less than the water solubility?

Statistical information:

(5) Is plot of C versus t at equilibration of zero slope?

Corroborative information: none.

Direct (aqueous) photolysis rate constant (k_d)

Chemicals in aquatic environments can be transformed by direct photolysis in sunlight. All chemicals are photodegradable under

suitable experimental conditions.[10] Direct photolysis in sunlight, therefore, can become an important process in the degradation path of chemicals in the environment.

Photoreactions are either direct or indirect. Direct photolysis involves light absorption by the chemical itself, whereas indirect photolysis is initiated through light absorption by natural components of the aquatic environment such as humic substances or microorganisms. Both processes may occur when a chemical is dissolved in water or sorbed to environmental particles. Light absorption and scattering due to this dissolved and particulate matter can significantly reduce the average direct photolysis rate constant in a natural water body. Moreover, indirect photoreactions in natural waters can greatly enhance light-induced reaction rates compared to direct photoreactions. The sum of the direct photolysis rate constant k_d and the indirect photolysis rate constant k_s is the net photolysis rate constant k_p, where k_d is often much larger than k_s, and k_p is essentially equal to k_d.

The rate constant k_d can be determined using artificial polychromatic light, with the advantage that results are more reproducible than outdoor studies. Unfortunately, it is difficult to extrapolate the results to the variety of outdoor conditions. Because of these difficulties, the best approach for screening studies is to use sunlight as the light source. Sunlamps, mercury-vapour lamps, and xenon lamps require some type of filtering to remove wavelengths of light below 290 to 300 nm. Pyrex glass has been the most popular choice in simulating the ozone filtering effect; however, its spectral transmittance is variable.

Values of k_d are commonly measured by exposing chemicals dissolved in pure water to sunlight and monitoring the decrease in concentration as a function of time. k_d is then the slope of $\ln(C_0/C)$ versus time, where C_0 and C are the concentrations at time zero and time t, respectively. Values for k_d determined with sunlight are applicable only to the specific study because sunlight intensity and distribution varies with season, latitude, time of day, cloud cover, water depth, and ozone layer.

Values of k_d can be estimated using the aqueous photolysis reaction quantum yield and the molar absorptivity.

Suggested unit: hr^{-1}.

Specific evaluation criteria for k_d:

Analytical information: none.

Experimental information:

(3) Was the chemical in aqueous solution exposed to sunlight?
(4) Are specifics stated on season, latitude, time of day and year, cloud cover, and temperature?
Was light, intensity determined during the experiment using:
(5) a. spectroradiometer or actinometer?
(3) b. broad band light meter?
(3) Is *pH* reported if chemical can ionize?
(2) Were reaction vessels capped?
(2) Was cosolvent (if used) inert?
(5) Were dark controls run to determine whether the chemical hydrolyzes, volatilizes, biodegrades and/or sorbs, and were these processes considered?
(5) In the case of a weakly absorbing system (absorbance <0.02), was the photoreaction studied at a minimum of two different concentrations to determine that the photolysis rate is first-order with respect to substrate concentration (i.e. was fractional conversion per unit time independent of concentration)?
(2) Were experiments run on different days?

Statistical information:

(5) Were at least six samples analyzed over time, evenly distributed over the curve?
(2) Is plot of $\log C$ vs. t a straight line (variability in sunlight intensity may cause the relation to be non-linear)?
(5) Was precision of k_d determined from three or more replicates and $< \pm 20\%$?

Corroborative information:

(4) Are sunlight k_d values close to k_d values estimated by using ϕ_r, ε_λ, and solar spectral irradiance?

Aqueous photolysis reaction quantum yield (ϕ_r)

Chemicals introduced into aqueous environments can undergo transformation by direct photolysis in sunlight into new chemicals with different properties from their precursors. ϕ_r is a useful and fundamental quantity in the study of photochemical reaction mechanisms and indicates the efficiency of a photochemical reaction by converting absorbed light into chemical reactions. It is expressed in terms of

moles of chemical reacted per einstein of light absorbed by the chemical:

$$\phi_r = \frac{\text{moles of chemical reacted}}{\text{number of einsteins absorbed}}$$

$$= \frac{\text{number of molecules reacted}}{\text{number of photons (quanta) absorbed}}.$$

ϕ_r is used to calculate the direct photolysis rate constant, where maximum quantum yield for direct photolysis of a chemical in dilute solution is one. A body of data supports the postulate that reaction quantum yields for direct photolysis are usually wavelength independent in water and are about the same in natural waters as in distilled water. Therefore, only a single quantum yield determination in air-saturated distilled water is necessary to compute direct photolysis rates. Rates of indirect photolysis are more difficult to compute because molar absorptivities and concentrations of natural photosensitizers are usually unknown.

One method of determining ϕ_r involves simultaneous irradiation of chemical and actinometer with monochromatic light of constant intensity. A chemical actinometer is a solution of some photoreactive reference compound that reacts with a well-defined reaction quantum yield, ϕ_R. The reaction mixture is kept at a constant temperature (25 ± 2 °C) in a merry-go-round photochemical reactor or a photochemical optical bench and provides fast and reliable measurements with a precision of about 10%. The irradiation is done in a wavelength region where the absorptivity can be precisely measured. At least six samples should be analyzed over time. The direct photolysis rate constant, $k_{d,\lambda}$, is computed from the plot of $\ln(C_0/C)$ versus time, where C_0 and C are the concentrations at time zero and time t, respectively, followed by computation of a light intensity term, I_λ, using actinometer data.

$$I_\lambda = \text{reaction rate}/\phi_R$$

where the reaction rate is defined in terms of moles per liter of some product formed per unit time, and the units of I_λ are expressed in

einsteins per liter per unit time. $\phi_{r,\lambda}$ is computed by:

$$\phi_{r,\lambda} = k_{d,\lambda}/(2.303 I_\lambda \varepsilon_\lambda b)$$

where ε_λ is the molar absorptivity of the chemicals at the wavelength of the monochromatic light and b is the cell pathlength.

Attention must be paid to the units of the various terms to make sure that they are compatible.

Another method requires simultaneous irradiation of chemical and actinometer in sunlight. The value obtained for ϕ_r is subject to a potentially larger error due to assumptions and the extended calculation required.

At present, there is no procedure for *a priori* estimation of ϕ_r values based on molecular structure.

Suggested unit: unitless ($0 \leqq \phi_r \leqq 1$).

Specific evaluation criteria for ϕ_r:

Analytical information: none.

Experimental information:

(3) Is *pH* reported if chemical was ionic?
(5) Was a well-defined actinometer used?
What light source was used in the experiment?
(5) a. Monochromatic light from monochromator?
(4) b. Monochromatic light isolated by chemical glassfilter in a photoreactor (merry-go-round)?
(3) c. Polychromatic light from an artificial lamp source with well-defined spectral irradiance?
(2) d. Sunlight?
(2) Were reaction vessels capped?
(2) Was cosolvent (if used) inert?
(3) Were light source and pathlength varied?
(5) In the case of a weakly absorbing system (absorbance <0.02), was the photoreaction studied at a minimum of 2 different concentrations to determine that the photolysis rate is first-order with respect to substrate concentration (i.e. was fractional conversion per unit time independent of concentration)?

Statistical information:

(5) Were at least six samples analyzed over time, evenly distributed over the curve?

(5) Was precision of ϕ_r determined from 3 or more replicates and $< \pm 20\%$?

Corroborative information: none.

Molar absorptivity (ε_λ)

Molar absorptivity is also called molar absorbancy index, absorption coefficient, and molar extinction coefficient and is a wavelength-dependent property of chemicals that is a measure of the probability that a chemical will absorb light at wavelength λ.

The molar absorptivity is given by the absorbance of a solution divided by the product of the optical path in centimeters and the molar concentration of the absorbing species. It is derived from the familiar Beer–Lambert law:

$$\varepsilon_\lambda = \text{absorbance } M^{-1} b^{-1}$$

where M is the molar concentration and b is the cell pathlength.

Other units may be used; however, the units must be given if the data are to be of value to others. Values of ε_λ at wavelengths between ultraviolet and infrared are used to calculate the direct photolysis rate constants of chemicals in pure water, where the energy in the ultra-violet region is the primary source for photodegradation (290 to 450 nm).

Values of ε_λ are determined with a spectrophotometer using monochromatic light of known wavelength. The Beer–Lambert law should hold for nearly all non-associated molecules in solution.

Suggested unit: $M^{-1}\,cm^{-1}$.

Specific evaluation criteria for ε_λ:

Analytical information:

(3) Is the analytical instrumentation described?

(2) If a cosolvent was used, was it nonabsorbing?

(4) Were absorbance measurements made between 290 and 800 nm?

Experimental information:

(3) Is *pH* stated if the chemical was ionic?
(4) Was ε_λ calculated using Beer–Lambert law?
(3) Was baseline zero determined?
(3) Was the chemical tested at a minimum of two different concentrations?
(2) Was the cell pathlength varied?
(4) Was stability of the chemical shown?

Statistical information: none.

Corroborative information: none.

HYDROLYSIS RATE CONSTANT

Hydrolysis refers to the reaction of an organic chemical (RX) with water resulting in net exchange of the group X for the OH^- group from the water. Because water is present in large excess and the concentration of H^+ or OH^- is buffered and essentially constant, the kinetics of hydrolysis are pseudo first-order at a fixed *pH*.

The hydrolysis reaction can be catalyzed by H^+ or OH^-, known as specific acid-catalyzed or specific base-catalyzed hydrolysis. Thus, only acid or base hydrolysis together with neutral water reaction needs to be considered, usually at *pH* values of 3–5, 7, and 9–11. The chemical should be tested at a concentration of less than half its solubility in water, usually less than 10^{-5} molar. Buffer concentrations should be about 0.005 molar to avoid buffer catalysis. A marked curvature in a plot of $\log C$ versus time or a low correlation coefficient indicates a non-first-order process or problems with measurements. The hydrolysis process should be checked for loss of the chemical by other processes such as sorption, volatilization, or biotransformation. A minimum of six to eight samples should be generated over a span of two to three half-lives. The composite hydrolysis rate constant, k_h, is calculated from:

$$k_h = k_{acid}[H^+] + k_{neutral} + k_{base}[OH^-]$$

where k_{acid} and k_{base} are the second-order acid-catalyzed and base-

catalyzed hydrolysis rate constants, respectively, and $k_{neutral}$ is the first-order neutral hydrolysis rate constant determined at *pH* 7.

Hydrolysis experiments should be performed in solutions maintained at constant and accurately measured *pH* and temperature. Cosolvents should be minimized ($<1\%$) because they can affect the hydrolysis rate constant. Hydrolysis values obtained from experiments conducted at a *pH* below 2 may not be accurate because of a decrease in the autoprotolysis constant. Hydrolysis studies at a high *pH* may experience sodium interference. Determination of the neutral hydrolysis rate constant is sometimes complex because acid or alkaline catalysis can overlap the *pH* 7 (neutral) measurement.

Suggested units: $M^{-1}\,hr^{-1}$ for k_{acid} and k_{base}

hr^{-1} for $k_{neutral}$.

Specific evaluation criteria for hydrolysis:

Analytical information: none.

Experimental information:

(4) Were reaction vessels capped with teflon liners, or glass-sealed ampules used for volatile chemicals?
(5) Was the rate determined in water and not in an organic/water mixture?
(4) Is an Arrhenius plot or corresponding data shown?
(4) Is the duration of experiment indicated through at least two half-lives?
(5) Was the chemical studied at a minimum of three *pH* values?
(3) Was the chemical studied at a minimum of two different concentrations?
(5) Was the chemical studied at a minimum of two temperatures?
(4) Was the hydrolyzing medium sterilized?
(3) Were bacterial plate counts done beyond five days of experiment?
(5) Was the *pH* kept constant and accurately measured?
(4) Is molarity of the buffer stated (is it high enough to maintain *pH* yet low enough to not catalyze the reaction)?
(3) Was a primary or a secondary *pH* buffer used?

Statistical information:

(5) Were at least six samples analyzed over time, evenly distributed over at least two half-lives?
(4) Is plot of $\log C$ vs. t linear?

Corroborative information: none.

BIOTRANSFORMATION RATE CONSTANT (k_{bio})

Biotransformation or biodegradation can give an estimate of the persistence of a chemical in a natural environment. It is one of the most important degradative mechanisms for organic compounds in nature but also the most complex and most difficult one for which to obtain environmentally realistic reaction rates. Variables that can affect the rate of biodegradation are: temperature, *pH*, salinity, dissolved oxygen, concentration of test chemical, concentration of degrading microorganisms, nutrients, trace metals, vitamins, and time. One of the lesser understood features of some biotransformations is that an acclimation period (or lag period) is observed before a significant population or organisms develops that can transform the chemical. The acclimation period may range from less than an hour to many months, after which the chemical may be transformed within a few hours.

Two systems are generally used to test biodegradability: die-away tests in static systems, and tests in flow-through systems (continuous cultures).

In the die-away test, the concentration of the test chemical is determined analytically as a function of time. In the flow-through system, a constant flow of the medium is fed into a completely mixed reactor. The degradation is calculated from the difference between the chemical concentrations in the inlet and effluent streams.

To define the kinetics of biotransformation independently of biomass, the second-order rate constant is required, either by using the concentration of the transforming bacteria or by assuming that all bacteria are transformers and stating this. Plate counts that are commonly used for biomass measurements account for more than just the transforming bacteria, and this value may represent only a fraction of the total bacteria or biomass present. Reports may describe biotransformation for suspended and/or attached organisms.

The second-order rate constant for suspended organisms incorporates the number of cells, whereas the second-order rate constant for attached organisms, or aufwuchs, may incorporate the number of cells or the ratio of number of cells to volume or the ratio of area to volume or even the ratio of total biomass (dry weight) to volume.

Evaluating biotransformation rate constant data becomes a difficult and complex task. Some of the features that are important in the evaluation process must include the types of organisms used in the measurement, whether pure or mixed cultures were used, how the second-order rate constant was calculated, and how an acclimation period was considered, if it occurred. The report should indicate whether the organisms utilize the chemical as a sole carbon energy source or not, which may depend on the concentration of the chemical.

Suggested unit: $L(\text{CFU})^{-1}\,\text{hr}^{-1}$ for suspended populations.

Specific evaluation criteria for k_{bio}:

Analytical information: none.

Experimental information:

(3) Was a lag period absent?
(5) If a lag period was observed, was the rate constant calculated from data collected after the lag period?
(3) Is the *pH* reported?
(3) Were cultures identified (pure versus natural)?
(4) Were bacterial populations constant and did not increase during the experiment?
(5) Was the chemical studied over at least two half-lives of decay?

Statistical information:

(5) Were at least six samples analyzed, evenly distributed over at least two half-lives?
(4) Is the plot of $\log C$ vs. t linear?
(4) Were replicate bacterial counts run?
(3) Is precision of bacterial counts reported?

Corroborative information: none.

CONCLUSION

In the assessment of health risk from pollutant exposure, it is most important to know the accuracy of fate data. Unfortunately, we

cannot evaluate this accuracy once a value has been published. We can, however, evaluate the documentation describing the value's experimental procedure. The system described here will evaluate this documentation for twelve rate and equilibrium constants. It can also be used, generally, to evaluate other properties. The Data Reliability Indicator (DRI) will tell the modeler the degree of confidence he/she can have in a literature value and thus provide guidance in selecting needed fate constants.

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References

1. ACS Committee on Environmental Improvement, *Anal. Chem.* **52**, 2242 (1980).
2. B. T. Bowman and W. W. Sans, *J. Environ. Sci. Health* **B18**(6), 667 (1983).
3. W. R. Mabey, J. S. Winterle, T. Podoll, H. Jaber, D. Haynes, D. Tse, V. Barich, A. Liu and T. Mill, Elements of a quality data base for environmental fate assessment. Final Report, EPA Contract No. 68-03-2981, SRI International Project 2073, Work Assignment No. 6, 1984.
4. Ph. H. Howard and G. W. Sage, Development of indicators of data documentation quality for environmental measurements data. Developed by the Syracuse Research Corporation, New York, for the Chemical Manufacturer's Association, Washington, D.C., under Contract 010114. 185, SRC F0089-01, 1986.
5. S. M. Creeger, N. K. Whetzel and C. L. Fletcher, Standard evaluation procedures: Hydrolysis, aqueous photolysis, aerobic soil metabolism, soil photolysis, soil column leaching. Report No. EPA 540/9-85-013, 014, 015, 016, 017. U.S. Environmental Protection Agency, Washington, D.C., 1985.
6. J. L. Lyman, W. F. Reehl and D. H. Rosenblatt, *Handbook of Chemical Property Estimation Methods* (McGraw-Hill Book Company, New York, 1982).
7. A. Albert and E. P. Serjeant, *The Determination of Ionization Constants* (Chapman and Hall, Ltd., London, 1971).
8. L. A. Burns, D. M. Cline and R. R. Lassiter, Exposure analysis modeling system (EXAMS): User manual and system documentation. Report No. EPA 600/3-82-023, U.S. Environmental Protection Agency, Athens, GA, 1982.
9. S. W. Karickhoff and D. S. Brown, Determination of octanol/water distribution coefficients, water solubilities and sediment/water partition coefficients for hydrophobic organic pollutants. Report No. EPA 600/4-79-032. U.S. Environmental Protection Agency, Athens, GA, April 1979.
10. R. G. Zepp, Experimental approaches to environmental photochemistry. In: *The Handbook of Environmental Chemistry* (O. Hutzinger, ed.) (Springer-Verlag, Berlin, Heidelberg, New York, 1982), Vol. 2, Part B, pp. 19–41.

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